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A THEORETICAL AND EXPERIMENTAL STUDY OF THE THERMOPHYSICAL PROPERTIES OF LITHIUM HYDRIDE

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I. THERMOPHYSICAL PROPERTIES OF LIQUID METALS AND HIGH-TEMPERATURE MELTS

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A THEORETICAL AND EXPERIMENTAL STUDY OF THE THERMOPHYSICAL PROPERTIES OF LITHIUM HYDRIDE

The work gives some results of a comprehensive study of LiH in its condensed and /7*
vapor phases. These studies were carried out at the Institute of High Temperature of
the Academy of Sciences of the USSR.

The caloric properties of the condensed phase were measured at a temperature
interval of 400-1,400° K by the mixing method using a calometer and an evaporating
liquid.

Results of the four series of experiments, treated by the method of the least
square, are approximated by the equations:
  solid phase

$$H_T - H_{273.15} = -1,691 \cdot 10^3 + 4,587T + 5,291 \cdot 10^{-3} \cdot T^2 \quad \text{cal/mole} \quad (1)$$

$$C_p = 4,59 + 10,58 \cdot 10^{-3} \cdot T \quad \text{cal/mole} \quad (2)$$

liquid phase

$$H_T - H_{273.15} = -7,330 \cdot 10^3 + 25,202T - 4,310 \cdot 10^{-3} \cdot T^2 \quad \text{cal/mole} \quad (3)$$

$$C_p = 25,20 - 8,62 \cdot 10^{-3} \cdot T \quad \text{cal/mole} \quad (4)$$

The melting heat according to (1) and (3) is equal to $\Delta H^{\text{пл}}_{962^\circ K}$ =5307 cal/mol. The
data error with enthalpy is about 0.7-0.8%, with heat capacity 2.5-3% and with
melting temperature 1.5%.

In the first phase lithium hydride dissociates into hydrogen and lithium by the
reaction LiH Li + 1/2H . Therefore, for the LiH - Li system, the usual p - N, i - N
and s - N diagrams are not appropriate.

This work calculates and constructs flat enthalpic and enthropic diagrams for
such a system using an "atomic" concentration a, determined in the following manner:

$$a = n_{aH}/(n_{aH} + n_{aLi}), \quad (5)$$

where n_{aH} and n_{aLi} are the number of hydrogen and lithium atoms respectively (in a pure
form and in LiH). The state of the system at p and T is determined by the value
$a_0 = n^0_{aH}/(n^0_{aH} + n^0_{aLi})$, , where n^0_{aH} and n^0_{aLi} are the complete number of H and Li atoms
p. 8
respectively in the system. It is clear that at a =1 the system is pure hydrogen,
at a =0 pure lithium, and at a =1/2 the system consists of stoichiometric lithium
hydride. The calculation was conducted on the premises that dissociation occurs only
in the gas phase, hydrogen in the liquid phase is insoluble and LiH and Li form the
ideal solution. In this case at any 0 < a < 1 the liquid phase consists of an Li and
LiH solution and the gas is a mixture of LiH, Li and H . It is easy to see that pure
lithium hydride in a liquid phase is impossible since the condition of phase
equilibrium requires the presence of lithium both in the liquid and gas phases. Let
us determine the atomic composition of the phases:

$$a' = n'_{aH}/(n'_{aH} + n'_{aLi}); \quad n'_{aH} = n'_{LiH}; \quad n'_{aLi} = n'_{LiH} + n'_{Li},$$

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*Numbers in margin indicate foreign pagination.

where n'_{LiH} and n'_{Li} are the number of LiH and Li moles respectively in the liquid phase. We will represent the molar shares of lithium hydride in the liquid phase with N:

$$N = n'_{LiH}/(n'_{LiH} + n'_{Li}), \quad a' = n'_{LiH}/(2n'_{LiH} + n'_{Li}).$$

From this we get

$$a' = N/(1 + N); \quad N = a'/(1 - a') \quad (6)$$

For the gas phase $n''_{aLi} = n''_{LiH} + n''_{Li}; \quad n''_{aH} = n''_{LiH} + 2n''_{H_2}.$ From this

$$a'' = \frac{n''_{aH}}{n''_{aH} + n''_{aLi}} = \frac{a_{LiH} + 2n_{H_2}}{2n_{LiH} + n_{Li} + 2n_{H_2}} = \frac{x_1 + 2x_3}{2x_1 + x_2 + 2x_3},$$

where x_1, x_2, x_3 are the molar shares of LiH, Li and H respectively in the gas phase, $\Sigma x_i = 1$. Then

$$a'' = (x_1 + 2x_3)/(2 - x_2). \quad (7)$$

It is clear that a' can change from 0 to 1/2, and a" from 0 to 1. From (7) in particular it is clear that a change back from the atomic to the molar composition in the gas phase is possible only taking the chemical equilibrium equation into consideration.

The system in its two-phase range is described by the following equilibrium equations:

$$x_1/N = p_{s_1}/p; \quad (8)$$

$$x_2/(1 - N) = p_{s_2}/p; \quad (9)$$

$$x_2/x_1 \cdot x_3^{1/2} = k_p/p^{1/2}, \quad (10)$$

where $\sum_{i=1}^{3} x_i = 1$. Here p_{s_1} and p_{s_2} is the saturation pressure of LiH and Li respectively, k_p is the constant of equilibrium of the dissociation reaction, p is full pressure. From the system of equations (8)-(10) we may obtain one equation for N (at the given T and p)

$$\left(\frac{1-N}{N}\right)^2 \left(\frac{p_{s_2}}{p_{s_1}}\right)^2 [N(p_{s_2} - p_{s_1}) + (p - p_{s_2})] = k_p^2.$$

Representing $(k_p \cdot p_{s_1}/p_{s_2})^2$ with $f_1(T)$, and p_{s_2} with p_{s_1} and replacing n with the atomic concentration $a' = N/(1 + N)$, we obtain

$$(1 - 2a')^2 \{a'f_2 + (1 - a')(p - p_{s_2})\} - f_1 a'^2(1 - a') = 0. \quad (11)$$

Solving this equation we obtain the atomic composition of the liquid phase a'. The atomic and molar compostions of the gas phase are obtained from the equations (8), (9) and (7).

It is easy to show that equation (11) has a solution at the necessary interval (i.e. $0 \leqslant a' \leqslant 1$) only at $p > p_{s_2}$. At $p = p_{s_2}$, a' = a" = 0 (pure lithium). At $p < p_{s_2}$

the system is one-phase and equation (7) makes no sense.

Pure lithium hydride (a' =1/2) in the liquid phase is obtained from (11) only if $p \to \infty$. This means that to obtain pure liquid LiH the reaction in the gas phase must be completely moved to the left. The dissociation pressure with pure hydride is practically final, but in any case it is much more that p_{s_1} and $P_{s_{2'}}$. This shows that the reaction actually occurs only in the gas phase and hydrogen is not soluble in a liquid. Sources give no indication of the solubility of hydrogen in lithium hydride.

Knowing the composition of the liquid and vapor phases we easily obtain the enthalpy and entropy of of the system on the line of saturation (provided that the solutions in the gas and liquid phases are ideal). Thus, we obtain the lines of saturations for i - a and s - a diagrams. If the compostion of the system satisfies the condition a' < a_0 < a" the system is two-phase. If a_0 < a' the system is one-phase (liquid). If a_0 > a" the system is overheated vapor. Calculation of a_0 < a' is trivial. For liquid $N = a_0/(1 - a_0)$.. If a_0 > a' the molar composition of the system is determined by the simultaneous solution of the equations (10) and (7) (taking the conditions $\sum_{i=1}^{3} x_i$ = 1) where a_0.

Since the weight enthalpy and entropy are a function of the atomic composition $a_{0'}$, the lever rule does not apply to i - a and s - a diagrams and the isotherms in the two-phase range are curved. Therefore the course of the isotherms in the two-phase range should be calculated separately. For this we must find the relationship of the degree of dryness x = g"/(g" + g') (where g' is the weight of the liquid phase, g" is the weight of the gas phase) and the composition $a_0 (a' < a_0 < a")$ on the isotherm at the given a_0

$$g' = n'[NM_1 + (1 - N) M_2],$$
$$g'' = n'' [x_1 M_1 + x_2 M_2 + x_3 M_3].$$

Table 1

Line of saturation

T, K	a'	a"	N'	$x_1^{\ast} \cdot 10^{\ast}$	$x_2^{\ast} \cdot 10^{1}$	$i^{\ast} \cdot 10^{-3}$ kcal·kg	$i^{\ast} \cdot 10^{-3}$ kcal/kg	$s^{\ast}$, kcal /kg dgr	$s^{\ast}$, kcal /kg dgr
						p = 0.3 atm			
1000	0,4103	0,9995	0,6958	0,008805	0,009678	—0,51617	2,4845	2,9056	20,833
1200	0,2676	0,9796	0,3653	0,2399	0,4152	0,33009	3,5994	2,9914	19,594
1400	0,12311	0,6794	0,1404	1,4742	4,744	0,95140	5,7524	2,9449	10,273
						p = 10 atm			
1000	0,4818	0,999995	0,9297	0,0003529	0,00006715	—0,90638	2,4718	2,9170	17,425
1200	0,4359	0,9997	0,7726	0,01522	0,004462	—0,34154	3,20227	3,1989	18,064
1400	0,3621	0,9955	0,5677	0,1788	0,05157	+0,25841	4,0095	3,3294	18,303
1600	0,2812	0,9699	0,3912	0,9534	0,4917	0,78379	4,9980	3,3695	16,921
1800	0,2041	0,8699	0,2564	2,9859	2,0375	1,2182	6,0169	3,3694	12,750
2000	0,1146	0,5069	0,1295	5,171	6,258	1,6139	6,6538	3,3134	7,6112

s, kcal/ kg dgr

kcal/kg
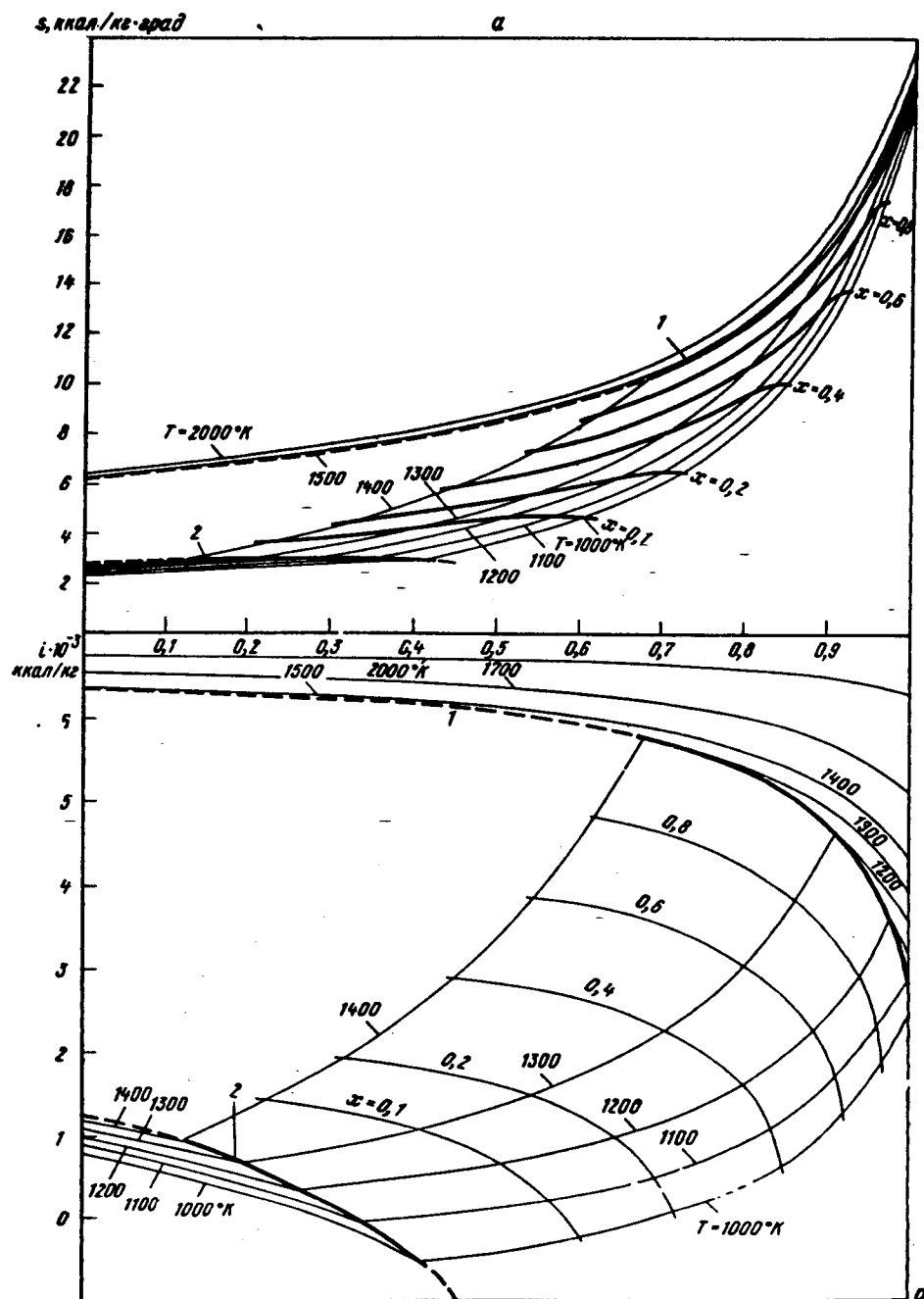
Diagrams of enthropy—composition and enthalpy—composition of system Li-LiH-H
a - p = 0.3 atm; b-p = 10 atm; 1 - line of condensation, 2- line of vapor formation

Here n' and n" are the total number of moles in the liquid and gas phases respectively, $M_1, \overline{M_2}, M_3$ are the molecular weights LiH, Li and H respectively.
Thus

$$x = \frac{NM_1 + (1 - N) M_3}{\frac{n'}{n''} [NM_1 + (1 - N) M_3] + x_1 M_1 + x_2 M_3 + x_3 M_3} . \qquad (12)$$

4

s, kcal/kg dgr

s, kcal/kg dgr

kcal/kg
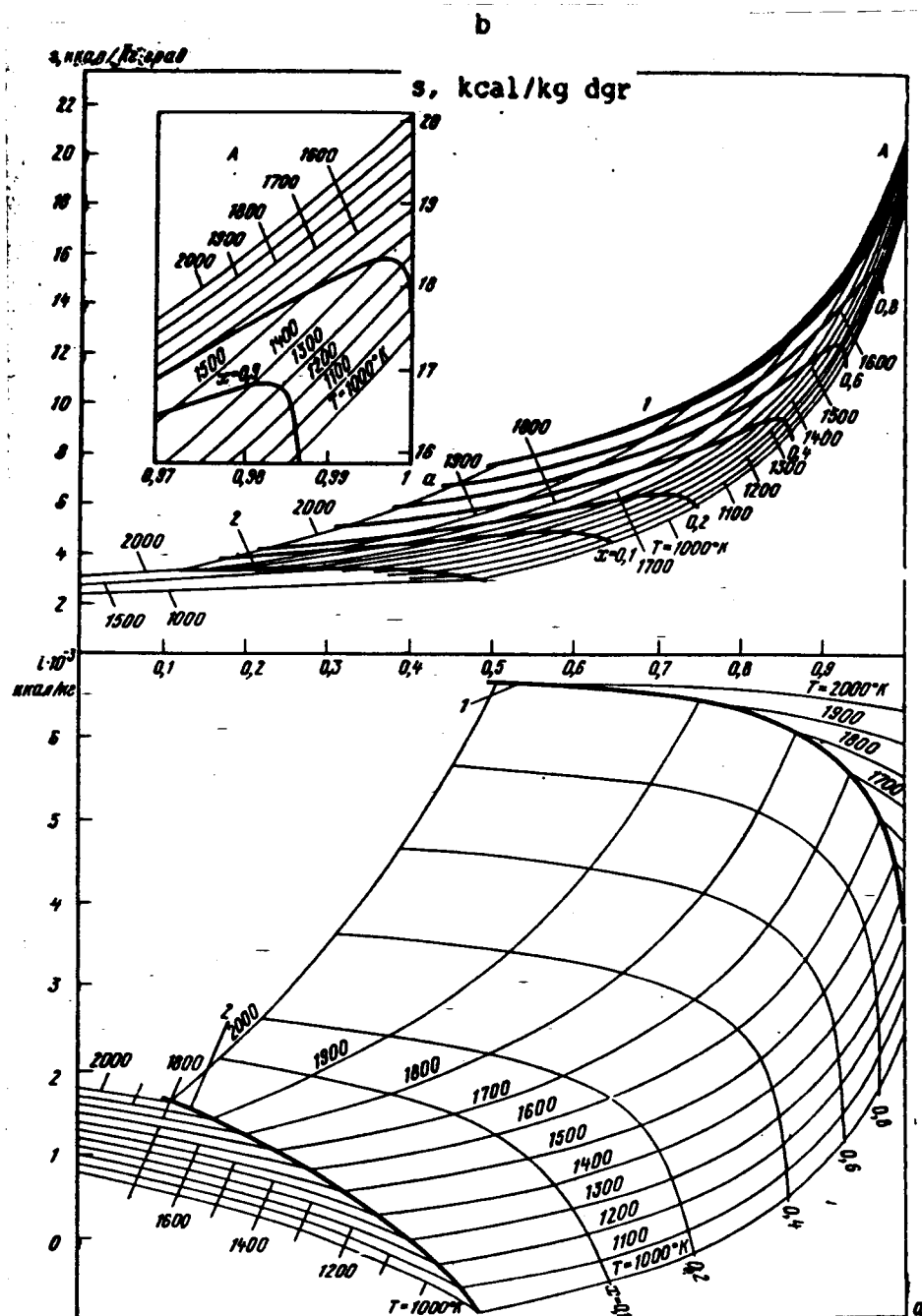
The connection between n'/n" and a_0 is easy to establish. Indeed

$$a_0 = \frac{n_{aH}}{n_{aLi} + n_{aH}} = \frac{n'_{LiH} + n''_{LiH} + 2n''_{H_2}}{n'_{LiH} + n''_{LiH} + 2n''_{H_2} + n'_{LiH} + n'_{Li} + n''_{LiH} + n''_{Li}} =$$

$$= \frac{Nn' + x_1 n'' + 2x_3 n''}{2Nn' + (1-N)\,n' + 2x_1 n'' + x_2 n'' + 2x_3 n''} = \frac{n'N + n''\,(x_1 + 2x_3)}{n'\,(1+N) + n''\,(2 - x_2)}.$$

Solving this equation for n'/n" and using the correlation of (2) and (3), we obtain

$$\frac{n'}{n''} = \frac{a'\,(2-x)\,(a''-a_0)}{N\,(a_0 - a_1)}. \qquad (13)$$

Table 2

Two-phase range

T°, K	x				
	0,1	0,2	0,4	0,6	0,8
			$p = 0,3$ atm		
1000	0,6054	0,7208	0,8511	0,9228	0,9682
	—0,21610	+0,083958	0,68408	1,2842	1,8843
	4,6984	6,4912	10,076	13,662	17,248
1200	0,5109	0,6508	0,8056	0,8892	0,9417
	0,65702	0,98396	1,6378	2,2917	2,9456
	4,6517	6,3120	9,6326	12,953	16,294
1400	0,2297	0,3166	0,4498	0,5470	0,6210
	1,4315	1,9116	2,8718	3,8320	4,7922
	3,6776	4,104	5,8760	7,3416	8,8072
			$p = 10$ atm		
1000	0,6426	0,7425	0,8599	0,9267	0,9699
	—0,5386	—0,23073	0,44491	1,1206	1,7962
	4,3678	5,8185	8,7201	11,622	14,523
1200	0,6185	0,7284	0,8542	0,9242	0,9688
	0,012879	0,3673	1,0761	1,7850	2,4938
	4,6854	6,1719	9,1449	12,118	15,091
1400	0,5773	0,7020	0,8406	0,9158	0,9631
	0,63352	1,0086	1,7588	2,5091	3,2593
	4,8268	6,3242	9,3190	12,314	15,309
1600	0,5088	0,6436	0,7961	0,8801	0,9332
	1,2052	1,6266	2,4695	3,3123	4,1551
	4,7246	6,0798	8,7901	11,500	14,211
1800	0,3795	0,501	0,6583	0,7557	0,8220
	1,6981	2,1780	3,1377	4,0975	5,0572
	4,3219	5,2584	7,1313	9,0043	10,877
2000	0,1736	0,2263	0,3166	0,3911	0,4537
	2,1179	2,6219	3,6299	4,6379	5,6458
	3,7431	4,1729	5,0325	5,8921	6,7516

Substituting (13) for (12) we obtain the relationship of the degree of dryness x and a_0 (at the given p and T).

Consequently, in all ranges of the state it is possible to calculate isotherms and construct flat enthalpic and enthropic diagrams for such a system. They were calculated using a 4 high-speed electronic computer. The constants and properties of individual components for the calculation were taken from data in this work and from known information monographs edited by V.P. Glushko and V.A. Kirillin. For each pressure we calculated 11 isotherms (from 1,000° to 2,000° K every 100°). We constructed diagrams for 8 pressures: 10^{-4}; 10^{-2}; 0.03; 0.1; 0.3; 1; 3; 10 bar. The extreme values of p were selected based on the following considerations: the minimum pressure should allow a phase shift by at least one isotherm, i.e. $p_{min} > (p_s)$ T = 1,000°; the maximum in any case should allow phase shifts by all isotherms, i.e.

Table 3

Gas phase

T°, K		a_0					
		0,2	0,4	0,6	0,8	0,9	0,99

p = 0,3 atm

T°, K		0,2	0,4	0,6	0,8	0,9	0,99
1200	$x_1 \cdot 10^2$						0,1095
	x_2						0,01872
	$i \cdot 10^{-3}$						3,3888
	s						20,628
1400	$x_1 \cdot 10^2$				1,1477	0,6901	0,08175
	x_2				0,3238	0,1755	0,01899
	$i \cdot 10^{-3}$				5,4376	4,9657	4,0954
	s				12,406	15,546	21,172
1600	$x_1 \cdot 10^2$	0,9988	1,272	1,269	0,9195	0,5534	0,06564
	x_2	0,8833	0,7421	0,5624	0,3257	0,1768	0,01915
	$i \cdot 10^{-3}$	6,4051	6,3077	6,1456	5,8129	5,4641	4,8212
	s	7,0008	7,9553	9,5172	12,657	15,881	21,656
1800	$x_1 \cdot 10^2$	0,8401	1,069	1,066	0,7731	0,4656	0,05527
	x_2	0,8842	0,7493	0,5638	0,3269	0,1776	0,01925
	$i \cdot 10^{-3}$	6,5723	6,5096	6,4060	6,1942	5,9728	5,5649
	s	7,0992	8,0742	9,6705	12,881	16,180	22,094
2000	$x_1 \cdot 10^2$	0,7327	0,9317	0,9295	0,6742	0,4062	0,04824
	x_2	0,8848	0,7442	0,5648	0,3277	0,1781	0,01932
	$i \cdot 10^{-3}$	6,7397	6,7126	6,6691	6,5820	6,4918	6,3267
	s	7,1875	8,1811	0,8091	13,085	16,454	22,496

p = 10 atm

T°, K		0,2	0,4	0,6	0,8	0,9	0,99
1600	$x_1 \cdot 10^2$						0,3277
	x_2						0,01656
	$i \cdot 10^{-3}$						4,8149
	s						18,360
1800	$x_1 \cdot 10^2$					2,417	0,2819
	x_2					0,1598	0,01701
	$i \cdot 10^{-3}$					5,9396	5,5595
	s					13,784	18,799
2000	$x_1 \cdot 10^2$			5,018	3,590	2,136	0,2498
	x_2			0,5356	0,3034	0,1624	0,01733
	$i \cdot 10^{-3}$			6,6283	6,5432	6,4627	6,3219
	s			8,3642	11,179	14,060	19,200

$p_{max} > (p_s^l)$ T = 2,000° . In calculation the spacing between a_0 was 0.05. Near the point $a_0 = 1$ the spacing was reduced because of the rapid curvature of the line of saturation and isotherms. We calculated the lines of constant dryness in the two-phase range x = const with spacing and x, equal to 0.1. In figures a and b i - a and s - a diagrams are given as an example. However, for converting the atomic composition into the molar for the gas phase the tables calculated by the chemical equilibrium equation must be used. Tables 1-3, corresponding to the diagrams of figures a and b are given with increased intervals of T, a_0 and x.

The collection gives results for studies of thermophysical properties of many liquids (hydrocarbons, metals, inorganic liquids). Some of the articles contain data of a methodical and methodological character: on viscosity, heat-carrying capacity, diffusion, P - V - T properties and caloric properties. They examine questions of current interest on the theory of the liquid state of substances: problems of phase transition, critical state etc. Some materials are devoted to methods of thermophysical experimentation.

The publicvation is directed toward a wide range of research and applied scientists: thermophysicists, engineers, technicians, instructors and students of physics, chemistry and technological departments of institutes of higher education.

Responsible editors

Doctor of Technological Sciences Professor Z.I. Geller,
Doctor of Physical and Mathematical Sciences L.P. Fillipov

This collection was compiled from materials of the IVth All-Union Thermophysical
Conference (Odessa, May, 1971) and includes reports read in the "Thermophysical
Properties of Liquids" section.

The large number of materials presented at the conference attests to the large
amount of research on the thermophysical properties of liquids in our country. The
collection includes materials not previously published that are important to the
growing demands of technology and that highlight the principal problems of the
thermodynamic behavior of liquids. Furthermore, some attention is devoted to new
methods of experimental and theoretical study of the thermophysical properties of
liquids.

The first section is devoted to the thermophysical properties of liquid metals
and is concerned with using them as specific heat carriers.

The second section examines some new works on studies of critical phenomena and
phase equilibrium. This section includes studies of compressibility and calculation
of P - V - T data using a digital computer, and investigates a single equation for
the state of liquid and gas-type neon.

Results of a study of heat conductivity and viscosity of hydrocarbons and
solutions as well as organic heat carriers is presented in the third section. It
also includs works discussing the contribution of the radiant component in the
effective coefficient of heat conductivity and some new methods of investigating
heat conductivity.

The fourth section examines works devoted to the study of the thermophysical
properties of freons.

The materials were edited by members of the department of engineering
thermophysics of the Odessa Technological Institute of the Refrigeration Industry
O.P. Ponomareva and B.B. Rogankov.

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16. Abstract

The work gives some results of a comprehensive study of LiH in its condensed and vapor phases. These studies were carried out at the Institute of High Temperature of the Academy of Sciences of the USSR. The caloric properties of the condensed phase were measured at a temperature interval of 400-1400°K by the mixing method using a calometer and an evaporating liquid. Results of the four series of experiments, treated by the method of the least square, are approximated by the equations.

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